Imidazo[4,5-f]-1,10-phenanthrolines:
versatile ligands for the design of metallomesogens

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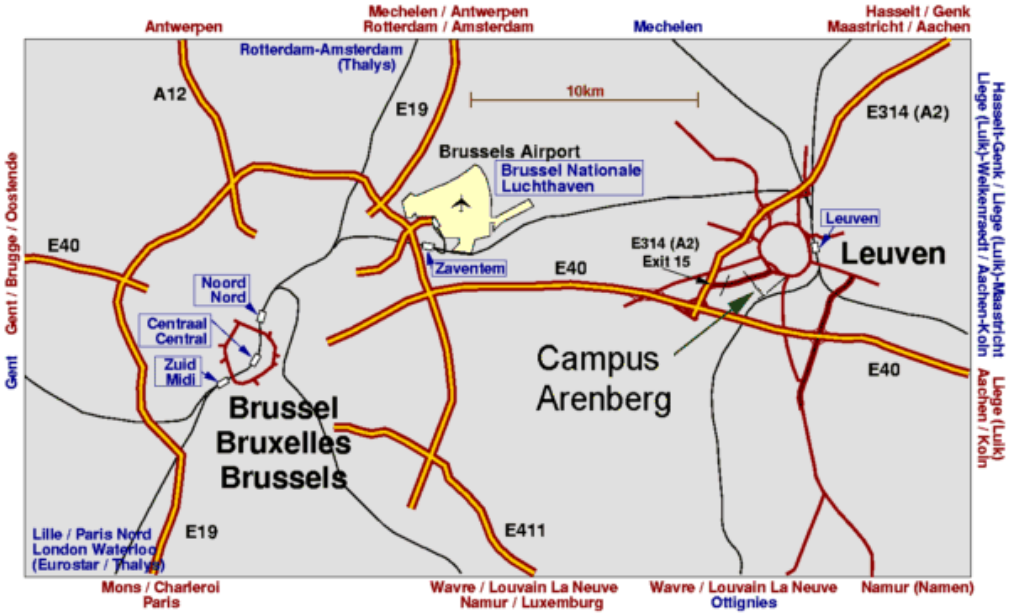
Leuven


Antwerpen
Mechelen / Antwerpen
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A12
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Luchthaven
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E40
Noord
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Campus
Arenberg
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Gent
Hasselt-Genk / Liege (Luik)-Maastricht
Liege (Luik)-Welkenraedt / Aachen-Koln
Liege (Luik)
Aachen / Koln
Lille / Paris Nord
London Waterloo
(Eurostar / Thalys)
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Mons / Charleroi
Paris
Wavre / Louvain La Neuve
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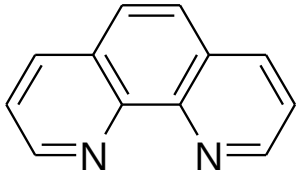
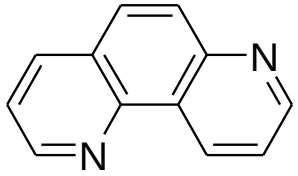
Namur (Namen)

K.U.Leuven, Department of Chemistry

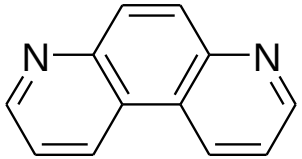
Phenanthrolines



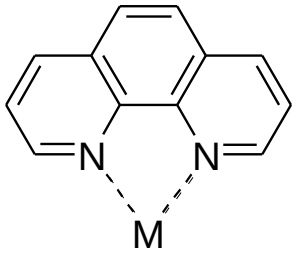
1,10-phenanthroline
(*o*-phenanthroline)

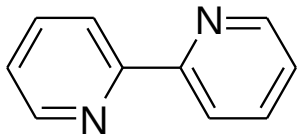


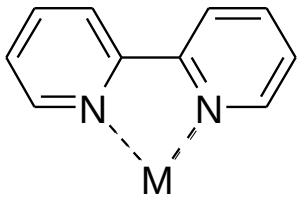
1,7-phenanthroline
(*m*-phenanthroline)



4,7-phenanthroline
(*p*-phenanthroline)

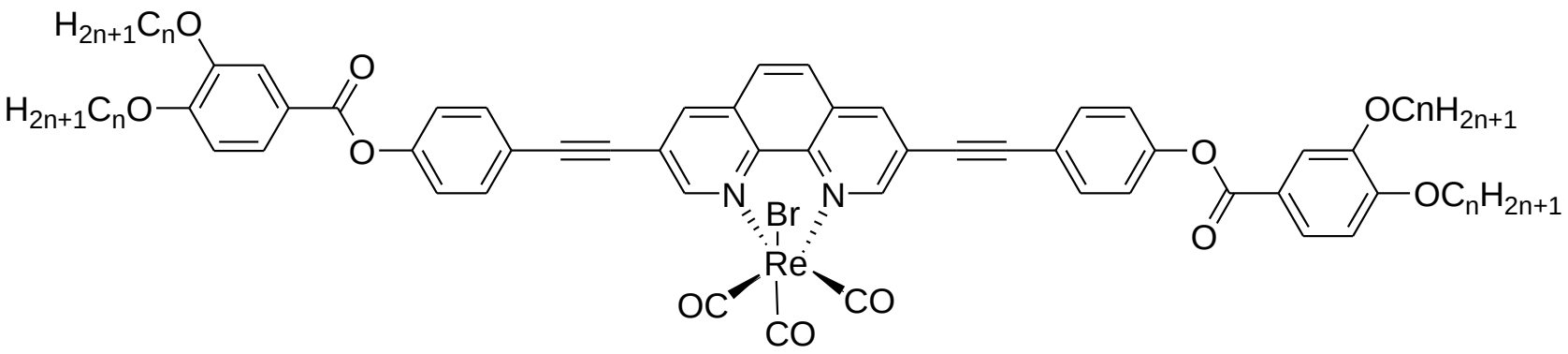






2,2’-bipyridine
(bipyridyl)

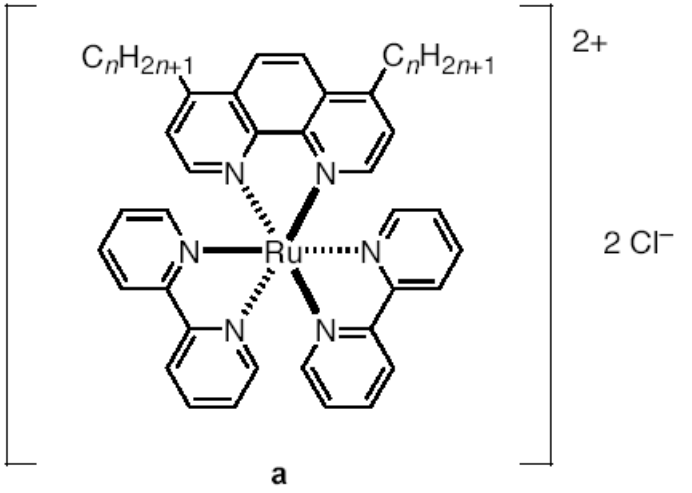
Metallomesogens derived of 1,10-phenanthrolines



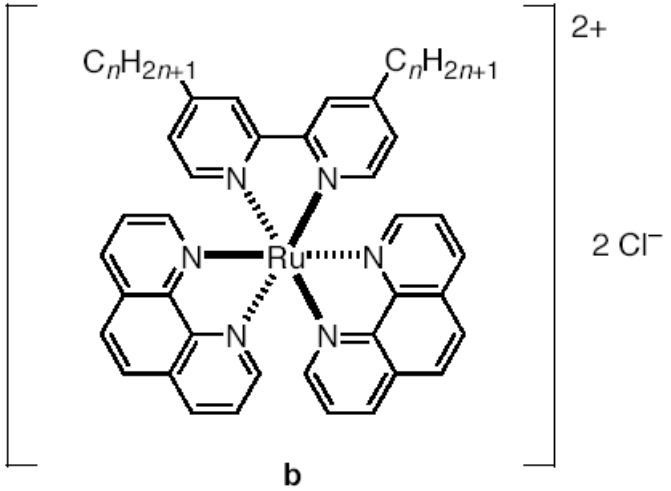
tetracatenar system; Col_h phases

Ref.: Date, R.W.; Iglesias, E.F.; Rowe, K.E.; Elliot, J.M.; Bruce, D.W. *Dalton Trans.* **2003**, 1914.

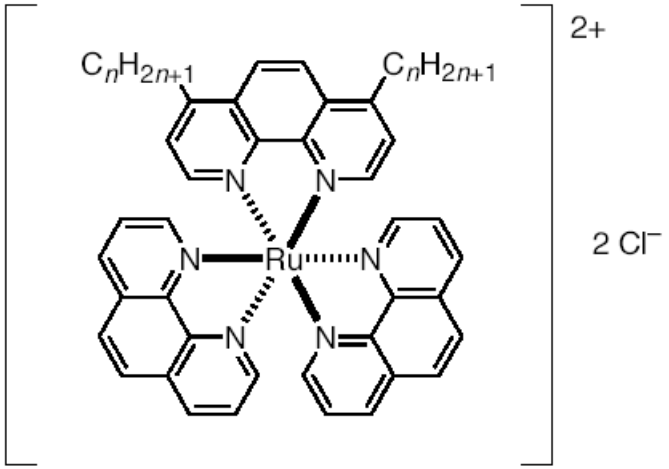
Lyotropic ruthenium(II) complexes



a



b



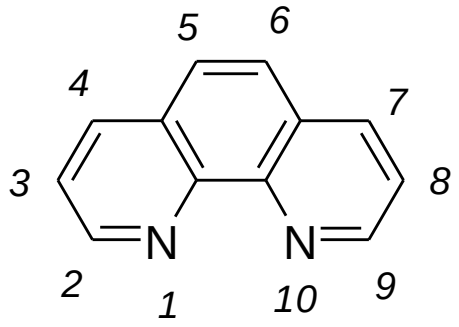
c

- hexagonal phase (H_1) in water
- used a a LC template for the synthesis of mesoporous silicates

Yam, V. W. W.; Li, B.; Zhu, N. *Adv. Mater.* **2002**, *14*, 719-722.

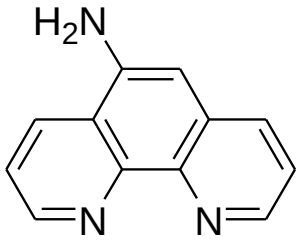
Our approach

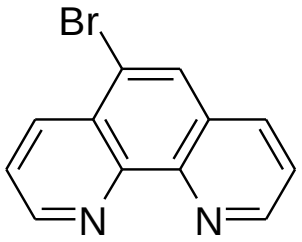
- 5,6 substituted 1,10-phenanthrolines

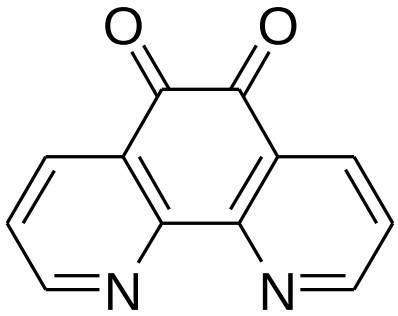


- The challenge was to find a model compound that can easily be substituted to induce mesomorphism.
- Not only simple alkyl chains, but also 4-cyanobiphenyl and cholesteryl groups.

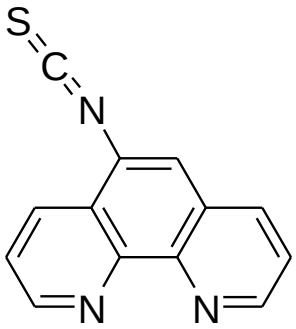
Possible building blocks

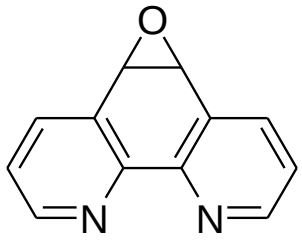




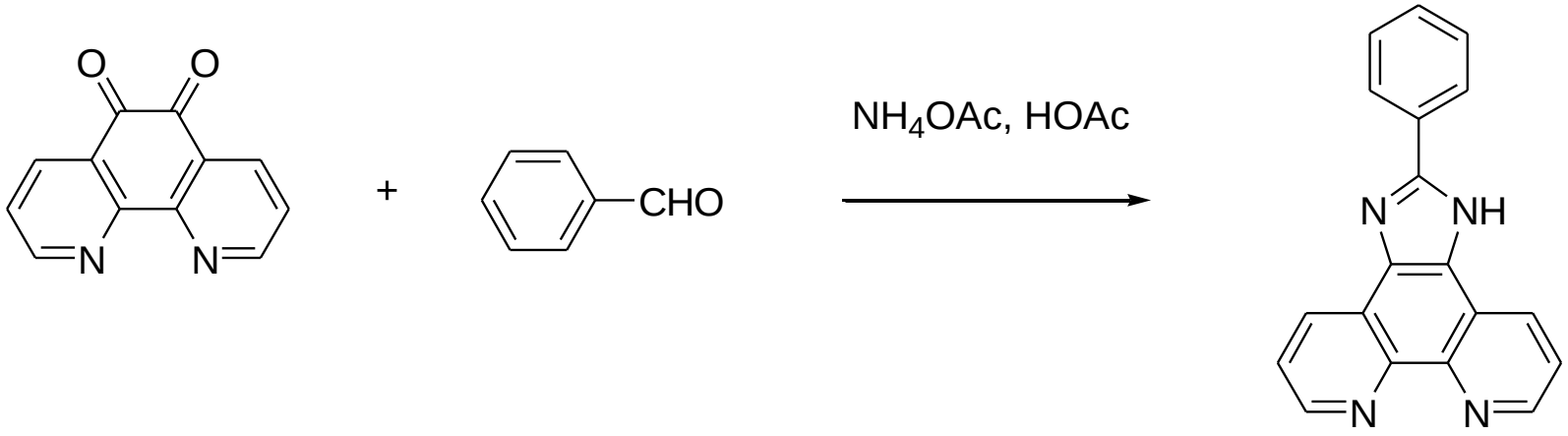


1,10-phenanthroline-5,6-dione





Imidazo[4,5-f]-1,10-phenanthrolines



Versatile system:

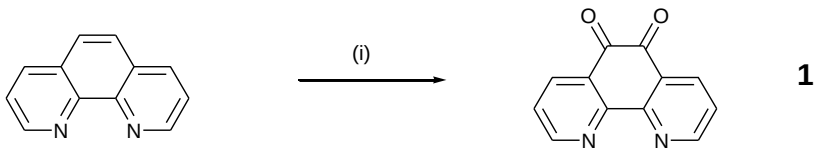
- benzaldehyde can be replaced by substituted benzaldehydes
- imidazole NH can be alkylated
- imidazole ring can be transformed to imidazolium ring by quaternization

Metallomesogens with decoupled mesogenic groups

- Design of high-coordination number metallomesogens (CN > 6) is a challenge, because of difficulties to obtain a sufficient shape anisotropy
- Increase of number of alkyl chains leads to columnar phases
- Concept: decoupling of metal-coordinating group and mesogenic group by a flexible alkyl chain (linker)
  $\Rightarrow$ formation of nematic phase is possible!

Ref.: T. Cardinaels et al., *Chem. Mater.* **17**, 6589-6598 (2005)

Synthesis of ligands



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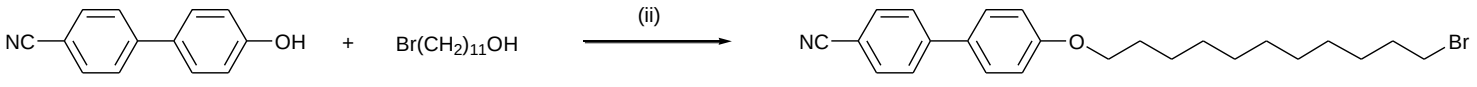

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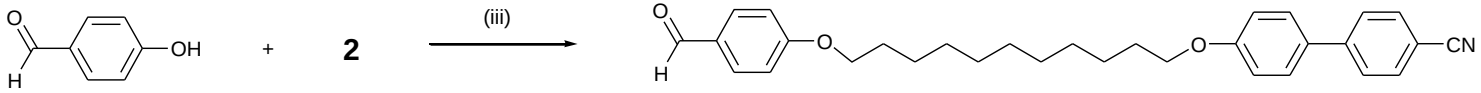

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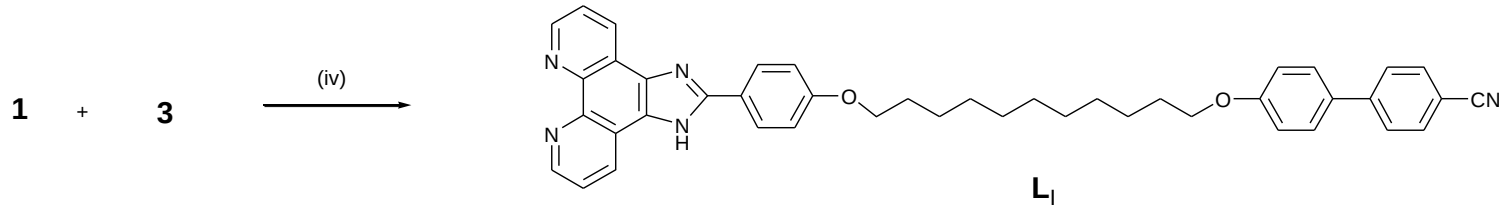
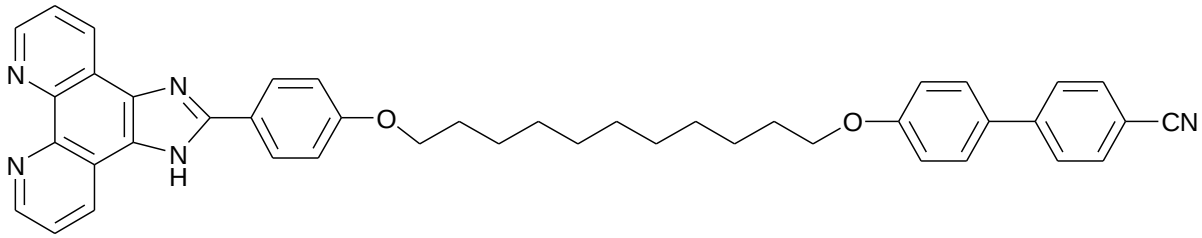


L_I

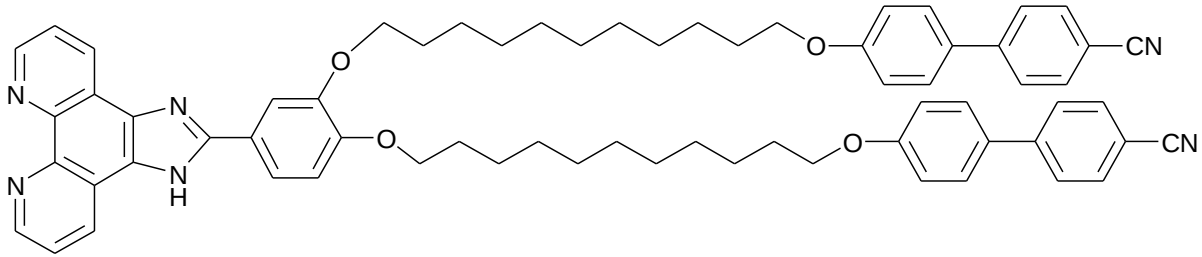
[a]Experimental conditions: (i) H_2SO_4/HNO_3, NaBr; (ii) PPh_3, DIAD, THF; (iii) K_2CO_3/KI, 2-butanone; (iv) NH_4OAc, HOAc.

Mesomorphism of ligands



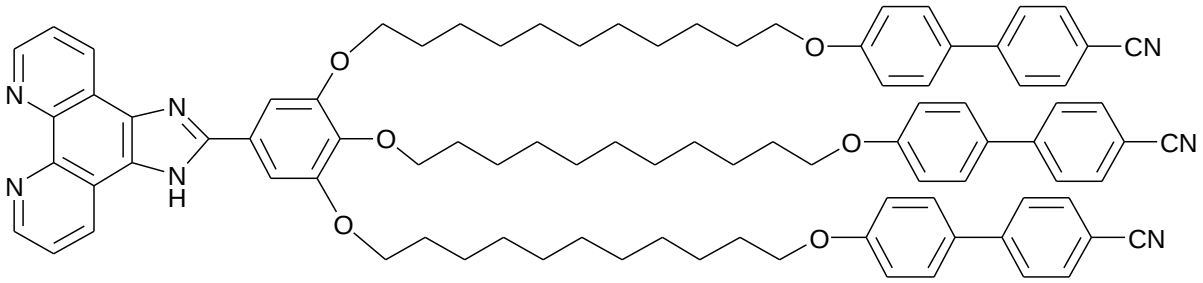
L_I

Cr · 80 · N · 124 · I



L_{II}

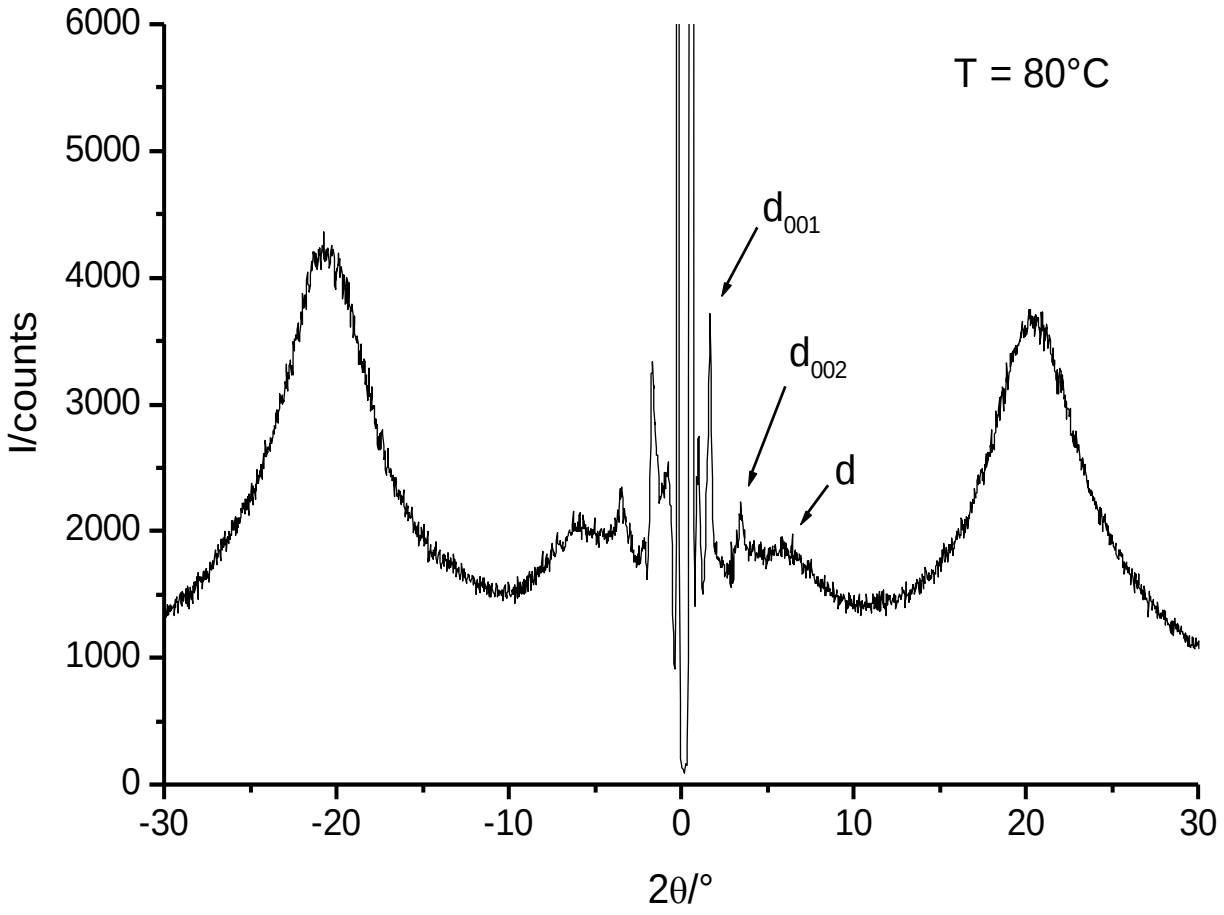
Cr · 75 · N · 128 · I



L_{III}

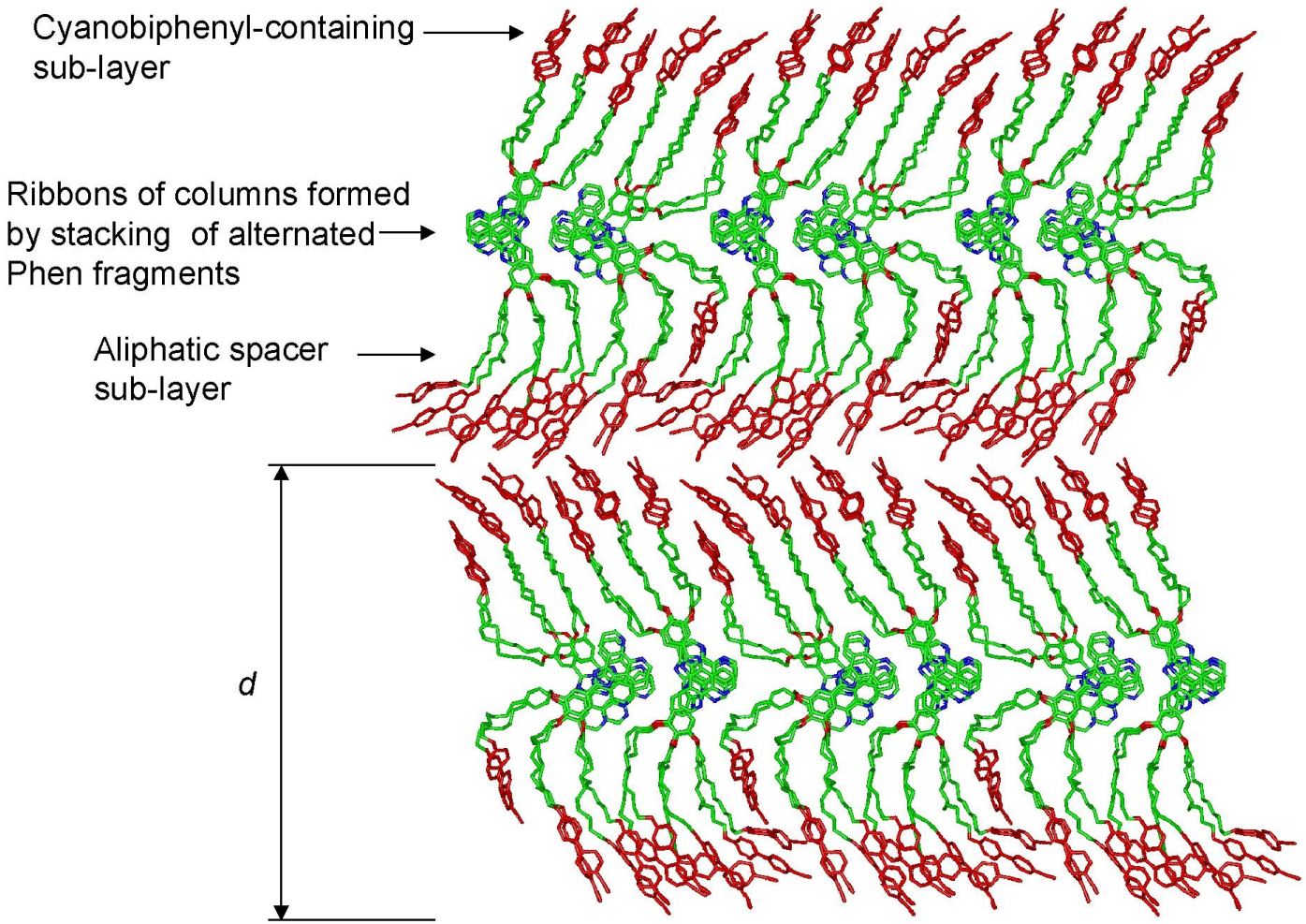
Cr · 48 · SmA_{Col} · 94 · I

X-ray diffractogram of ligand L_{III}

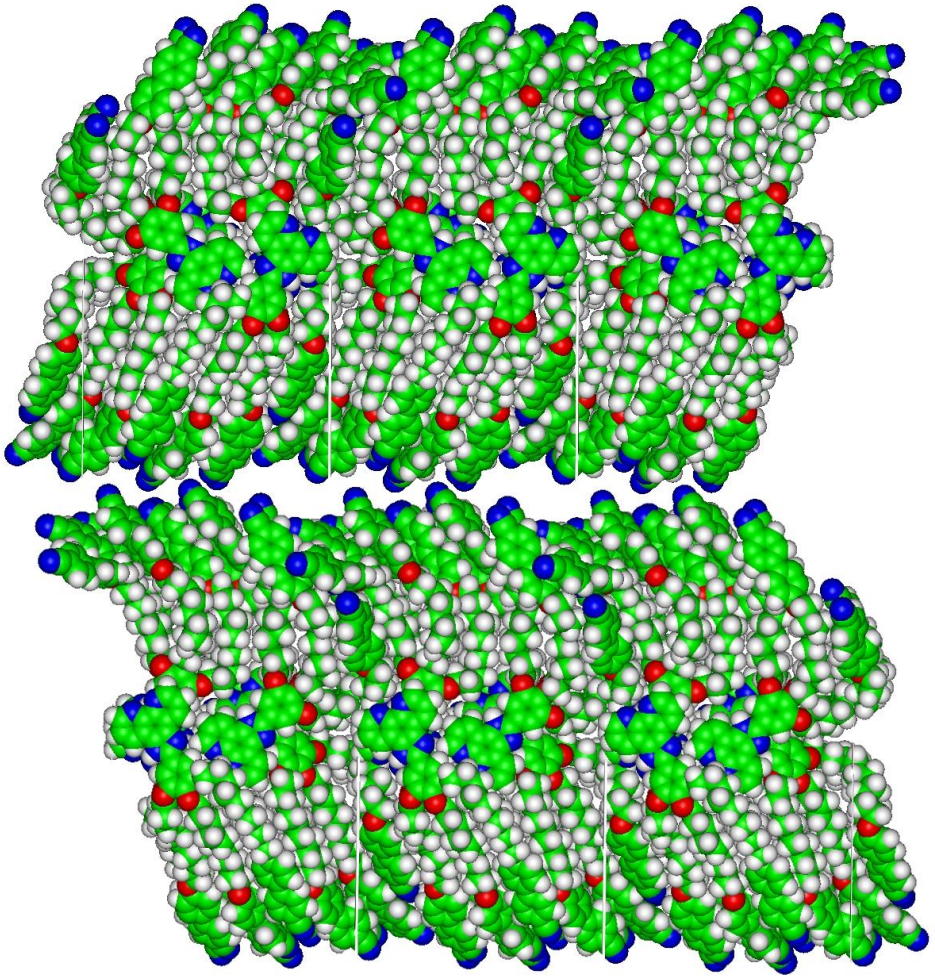


Lamellar columnar phase (SmA_{col})

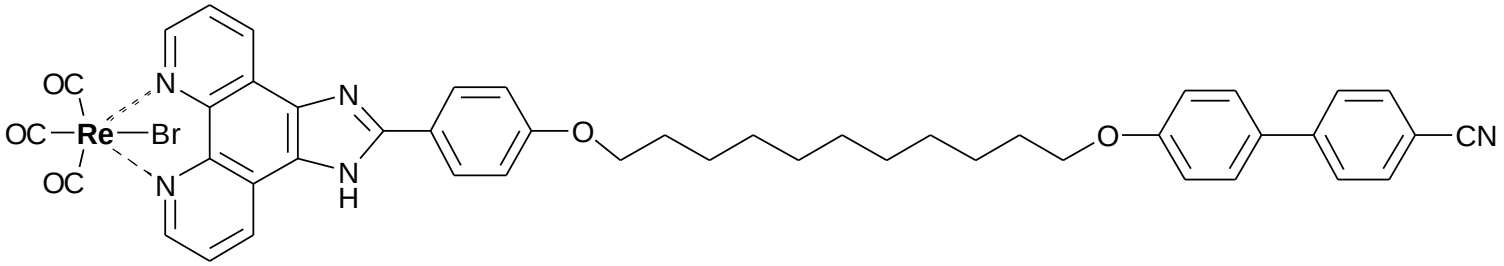
SmA_{col} phase of ligand L_{III}



SmA_{col} phase of ligand L_{III}



Rhenium(I) complex of ligand L_I

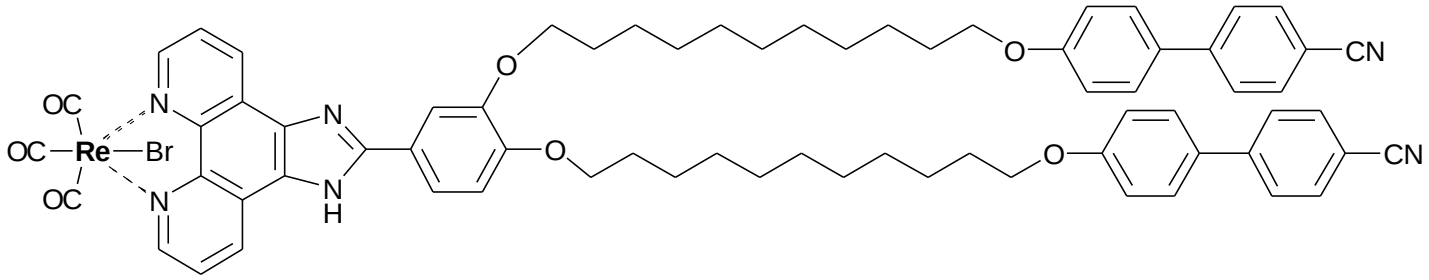


$[ReBr(CO)_3\ \mathbf{L}_I]$

Cr · 260 (· N · 158) · I

Monotropic nematic phase

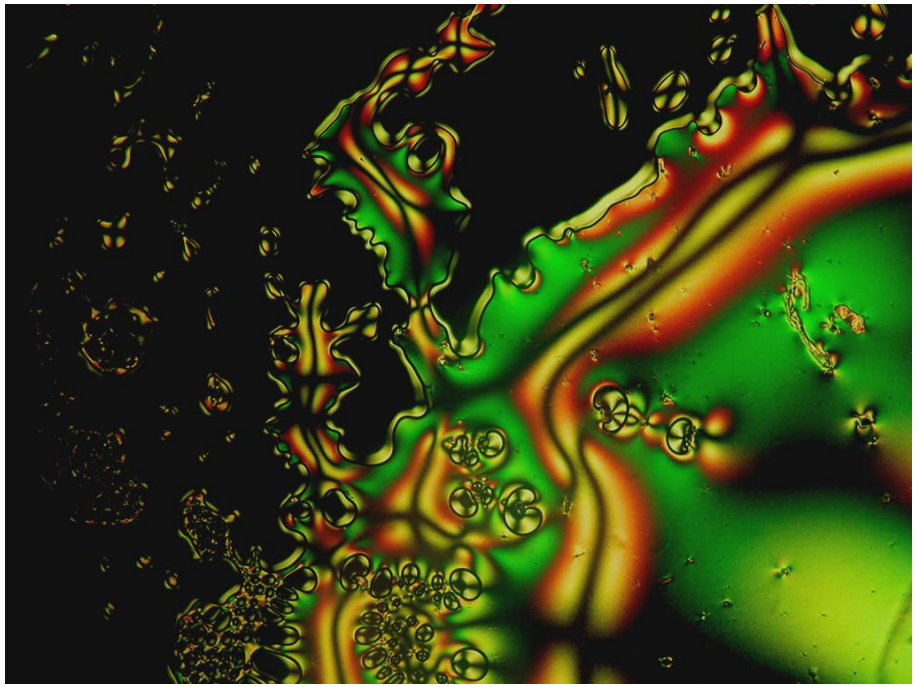
Rhenium(I) complex of ligand L_{II}



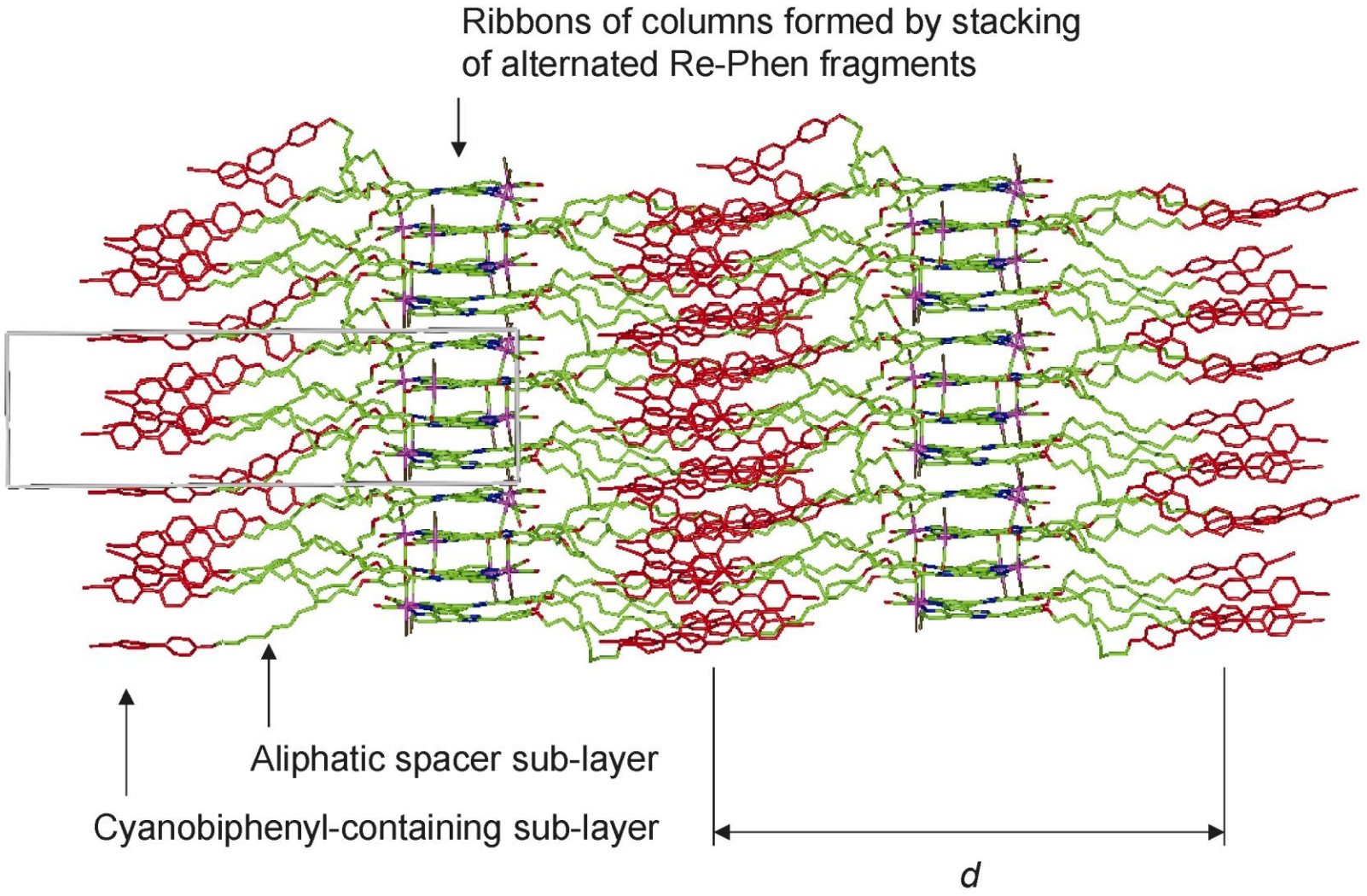
$[ReBr(CO)_3\ \mathbf{L}_{II}]$

$Cr \cdot (\ SmA_{Col}\ 65)\ 81 \cdot N \cdot 128 \cdot I$

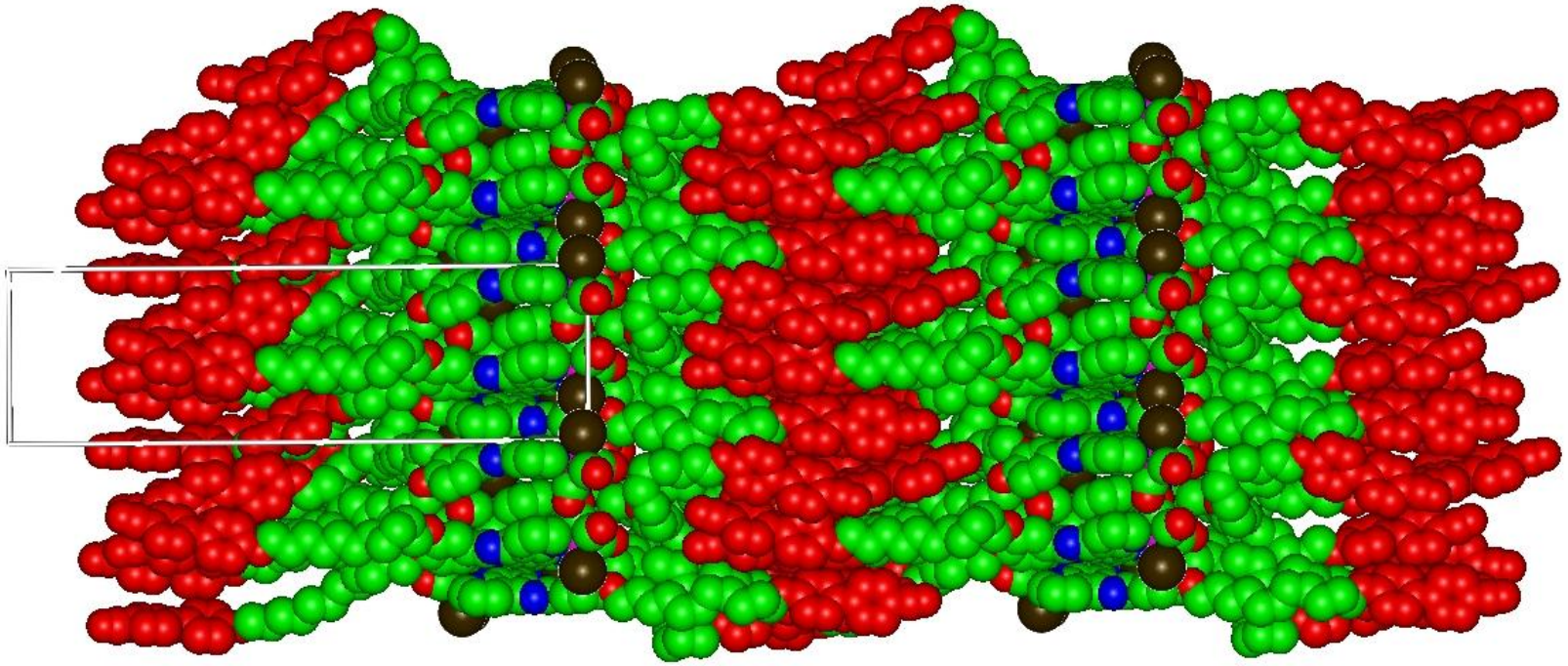
Nematic phase (N)
Lamellar columnar phase (SmA_{col})



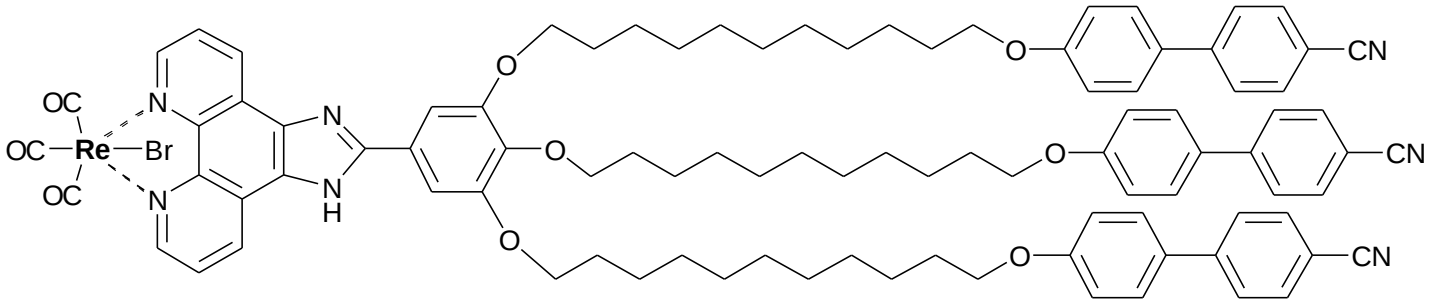
Packing of $[ReBr(CO)_3L_{II}]$ in the SmA_{col} phase



Packing of $[ReBr(CO)_3L_{II}]$ in the SmA_{col} phase



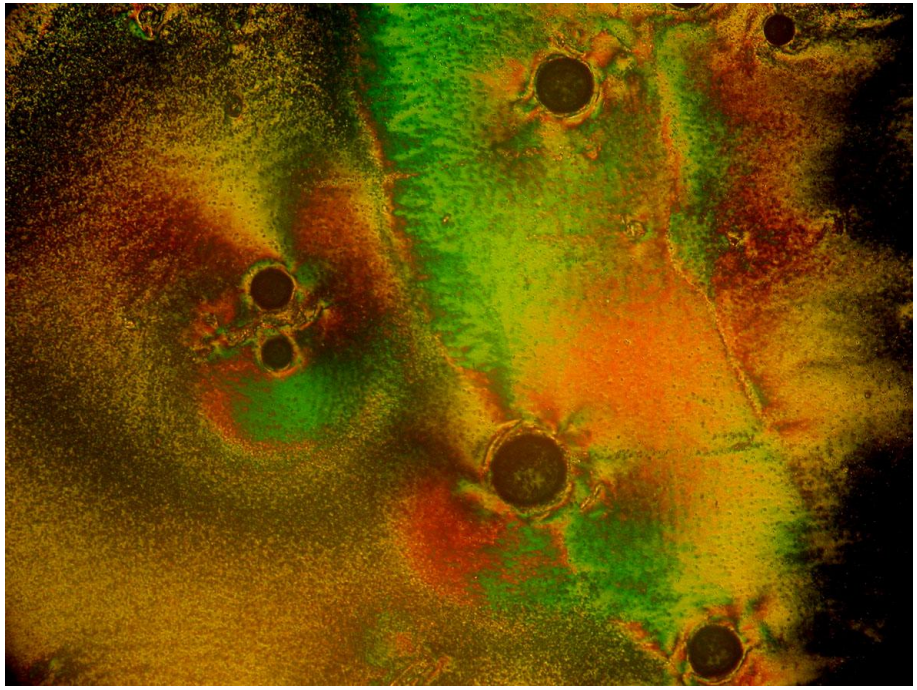
Rhenium(I) complex of ligand L_{III}



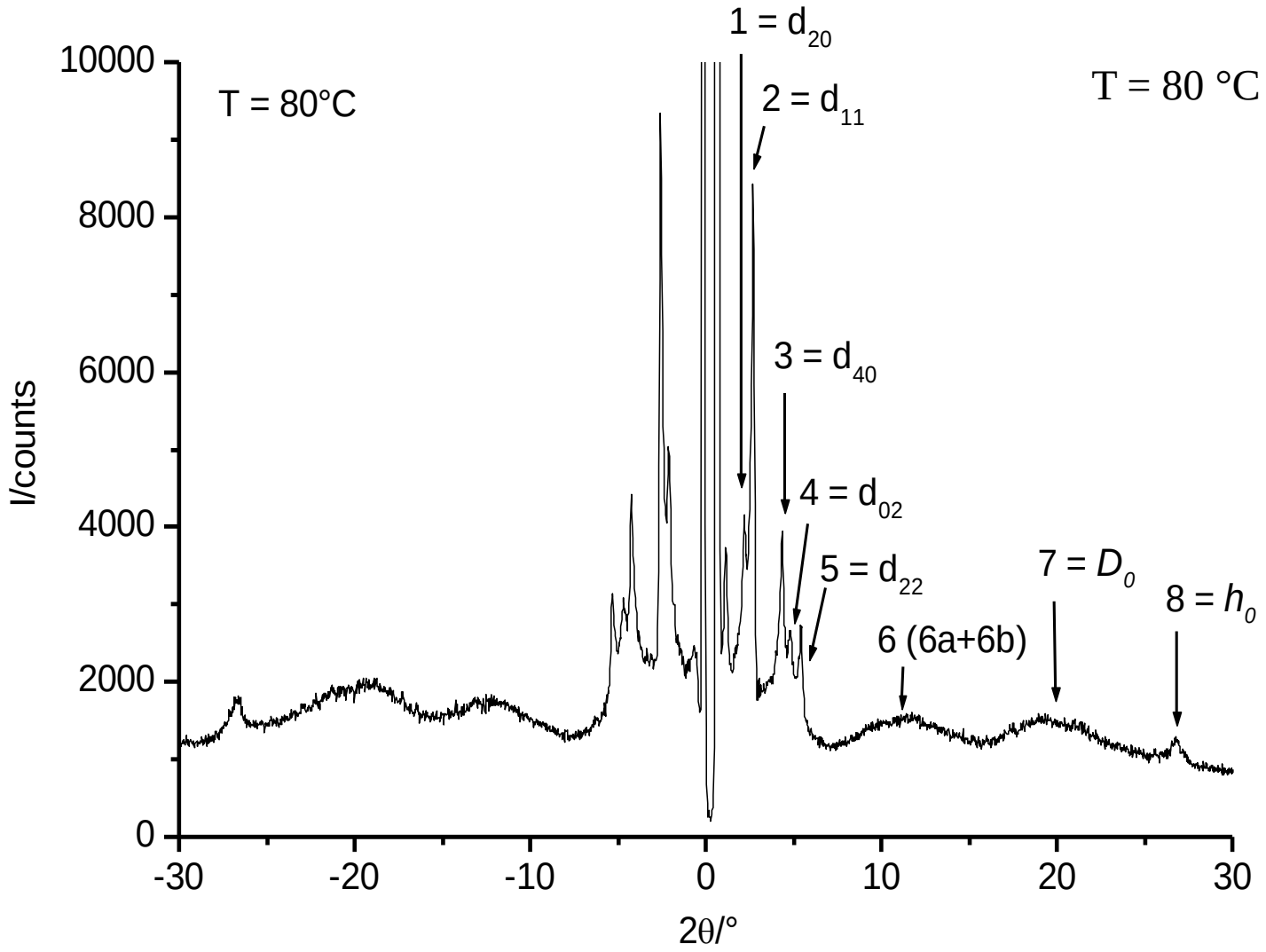
$[ReBr(CO)_3\mathbf{L}_{III}]$

Cr · 49 · Col_rL · 105 · I

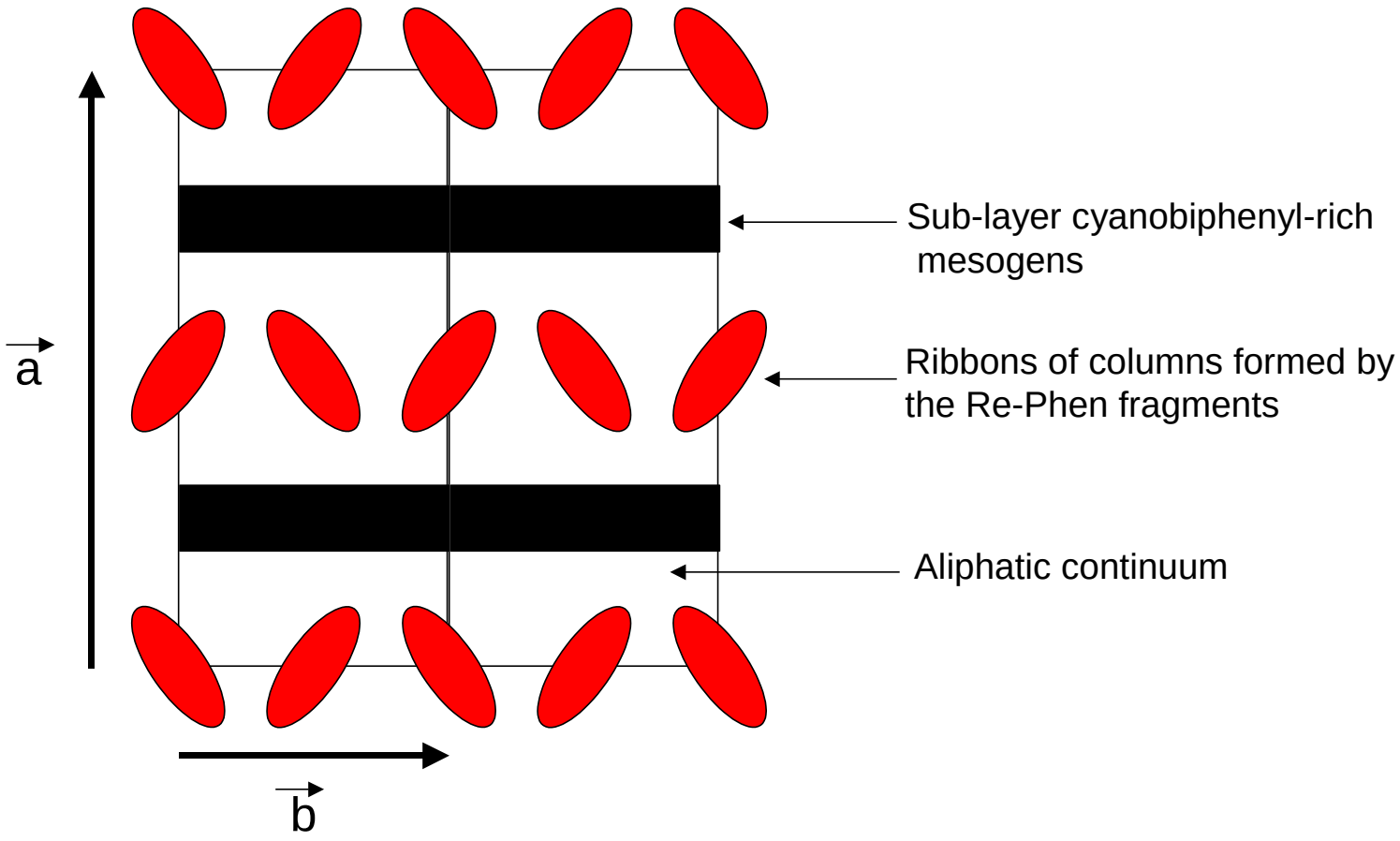
Lamellar columnar phase



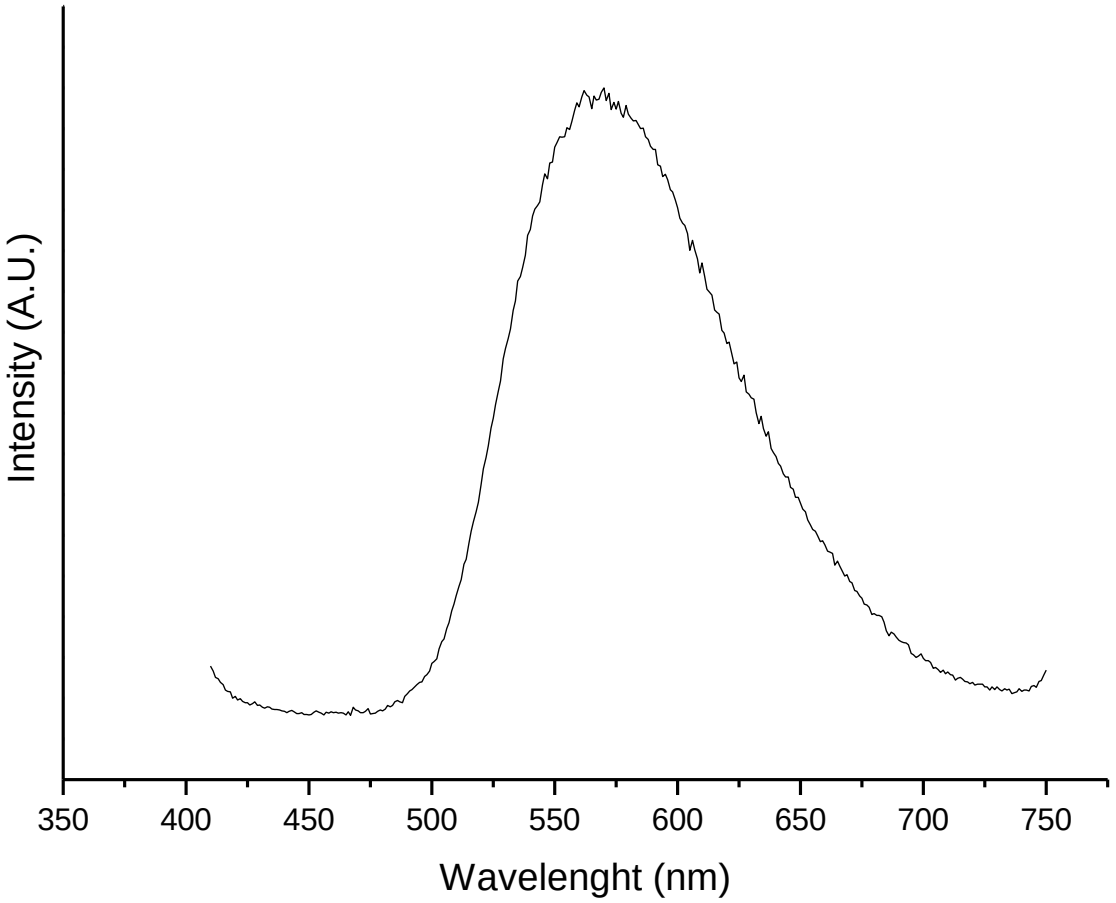
X-ray diffractogram of $[ReBr(CO)_3L_{III}]$



Lamello-columnar phase of $[ReBr(CO)_3L_{III}]$

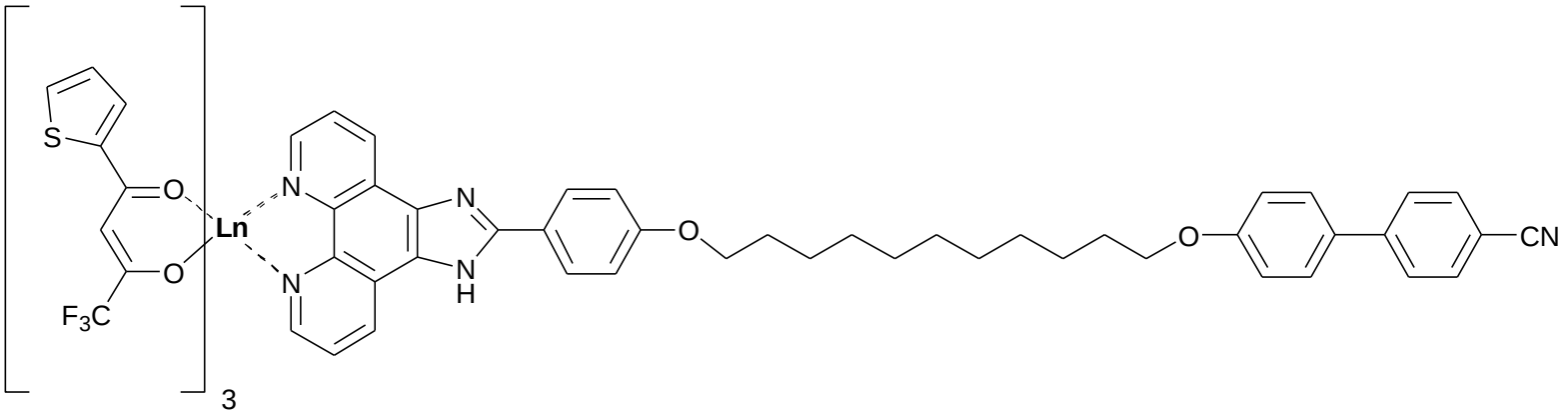


Luminescence spectrum of $[ReBr(CO)_3L_{II}]$



Vitrified mesophase, room temperature
Excitation wavelength = 385 nm
yellow emission, metal-to-ligand charge transfer (MLCT)

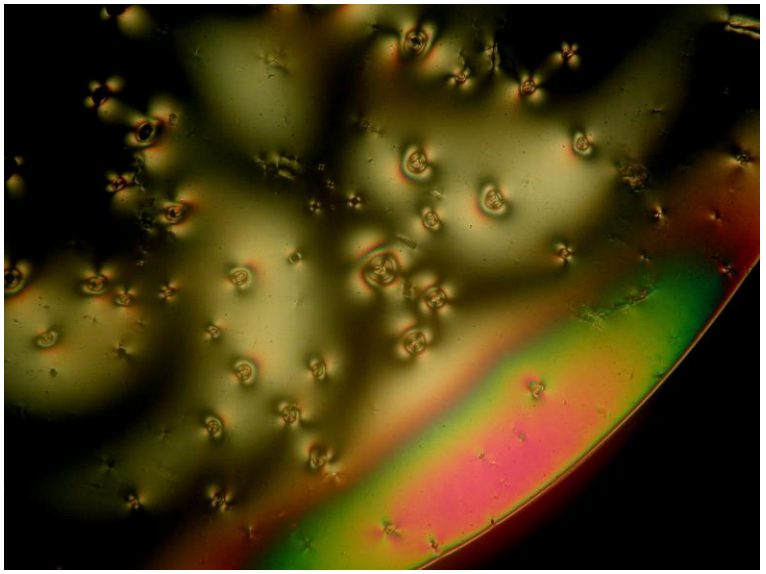
Nematic lanthanide complexes



$\mathbf{L}^4$ Cr · 80 · N · 124 · I

$[Nd(tta)_3\mathbf{L}^4]$ Cr · 86 · N · 138 · I

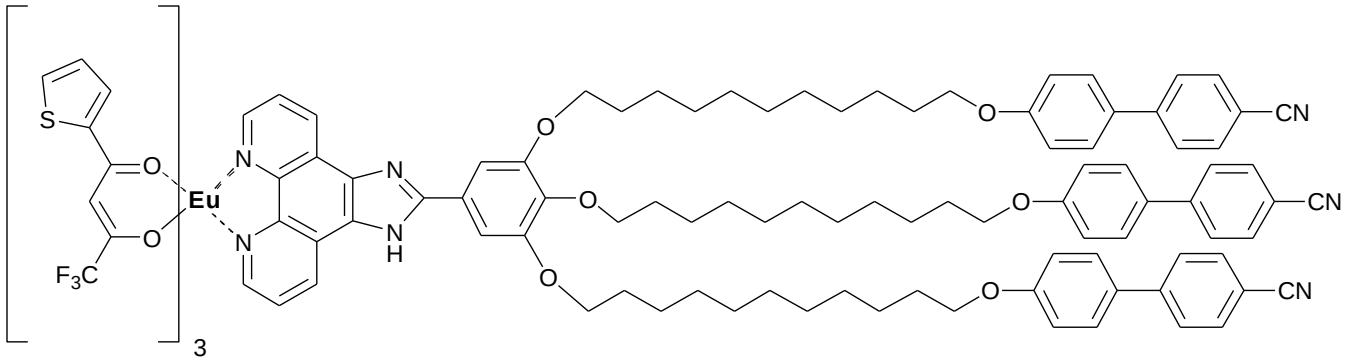
$[Eu(tta)_3\mathbf{L}^4]$ Cr · 89 · N · 138 · I



Nematic lanthanide complexes

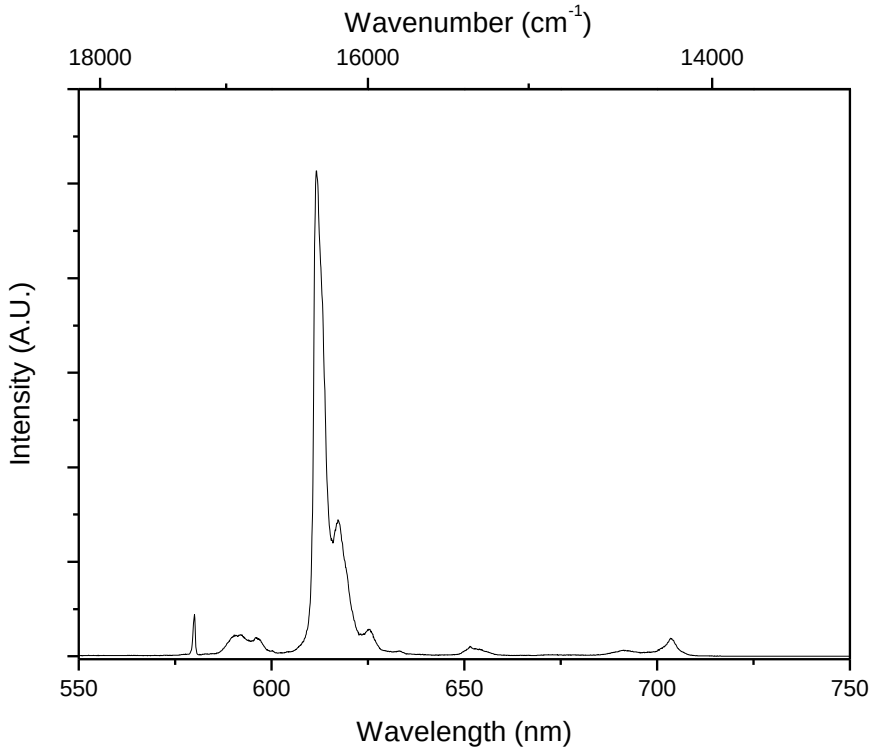
$[Y(tta)_3\mathbf{L}^{3,4}]$	Cr · 89 · N · 127 · I
$[La(tta)_3\mathbf{L}^{3,4}]$	Cr · 84 · N · 124 · I
$[Nd(tta)_3\mathbf{L}^{3,4}]$	Cr · 85 · N · 124 · I
$[Sm(tta)_3\mathbf{L}^{3,4}]$	Cr · 86 · N · 124 · I
$[Eu(tta)_3\mathbf{L}^{3,4}]$	Cr · 86 · N · 125 · I
$[Er(tta)_3\mathbf{L}^{3,4}]$	Cr · 90 · N · 127 · I
$[Yb(tta)_3\mathbf{L}^{3,4}]$	Cr · 92 · N · 127 · I

Nematic lanthanide complexes

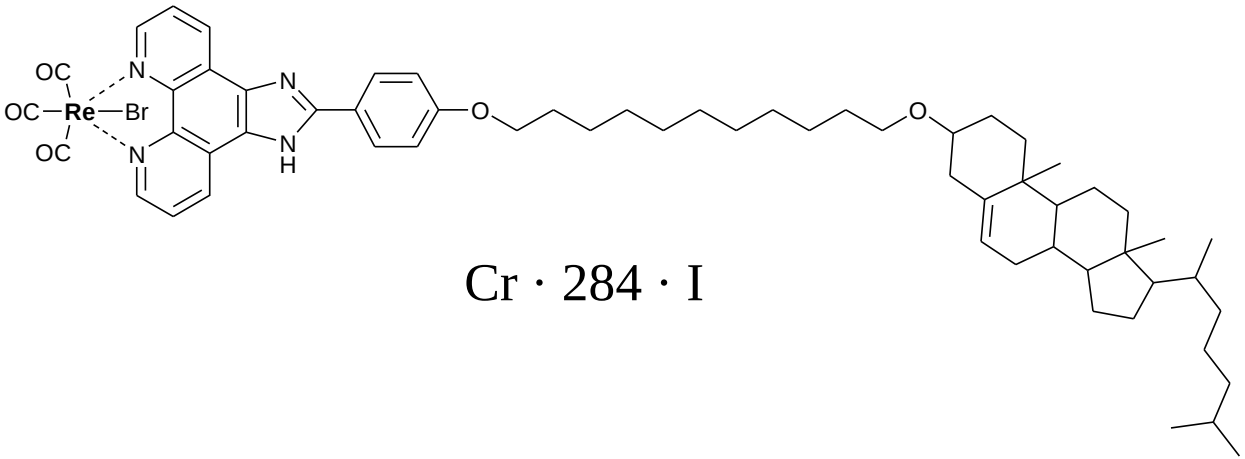


$[Eu(tta)_3\mathbf{L}_{III}]$ Cr · 83 · N · 92 · I

- intense red photoluminescence in solid phase
- good solubility in nematic host matrices (e.g. 5CB)

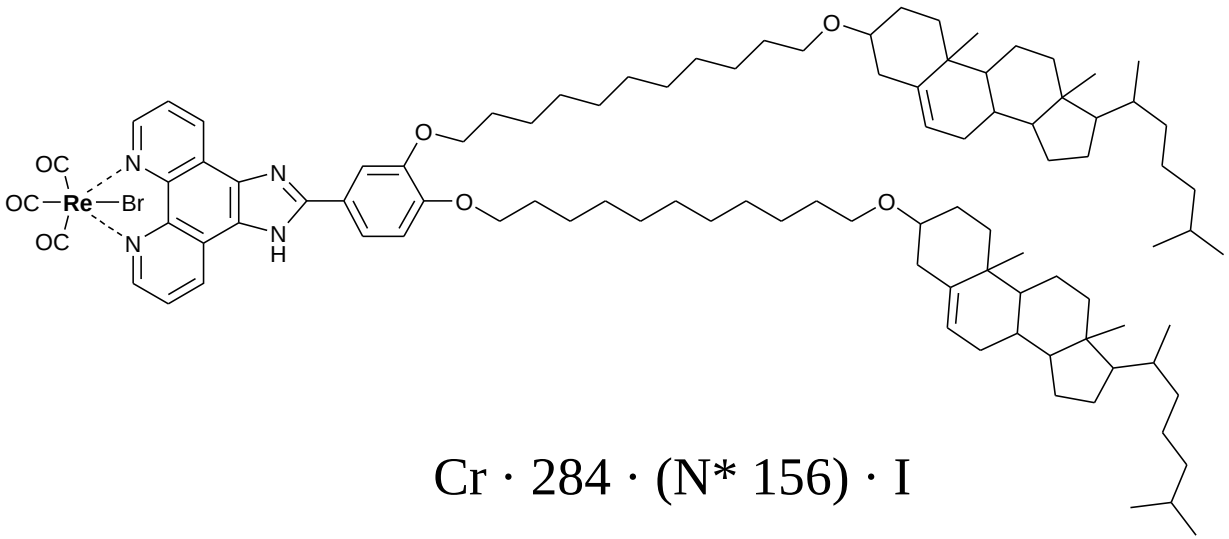


Complexes of cholesteryl-containing ligands



Cr · 284 · I

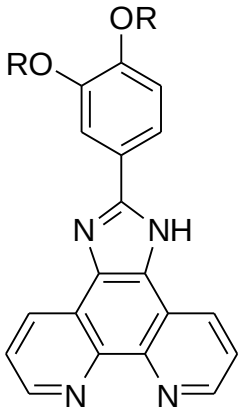
not a liquid crystal

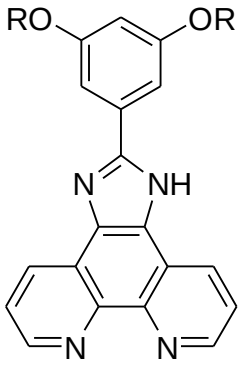


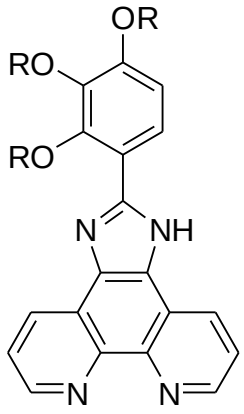
Cr · 284 · (N* 156) · I

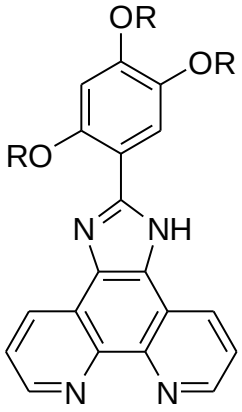
liquid crystal
monotropic N*

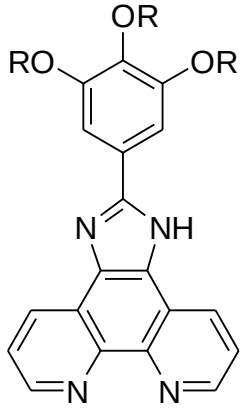
Alkoxy substituted 2-phenyl-imidazo[4,5-f]-1,10-phenanthrolines





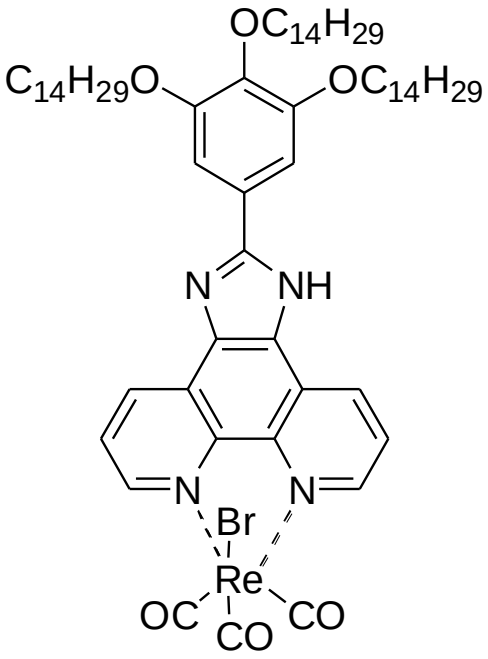




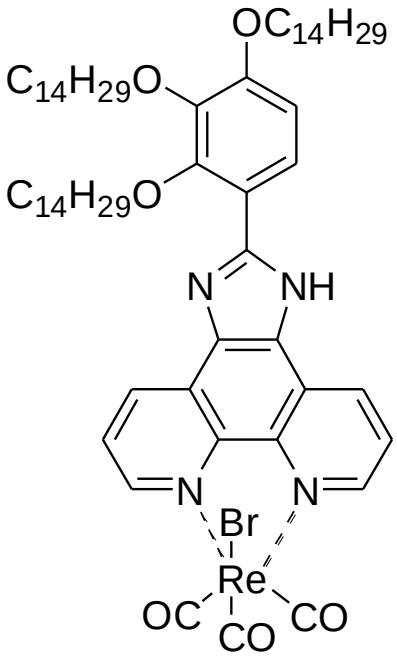


R = C_2H_5, C_6H_{13}, $C_{10}H_{21}$, $C_{14}H_{29}$, $C_{18}H_{37}$

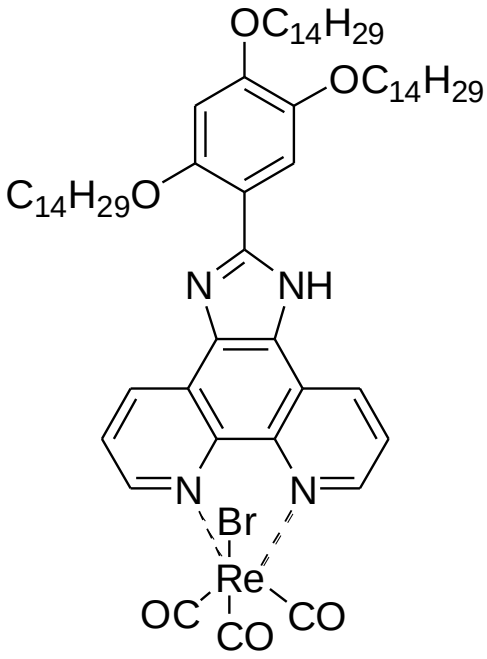
Complexes of alkoxy-substituted ligands



Cr · 91 (Col_h 89) · I

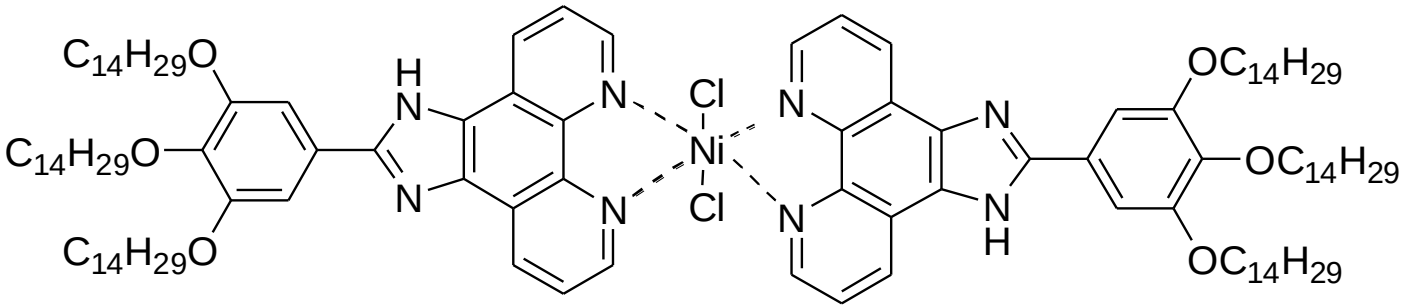


Cr · 180 · I



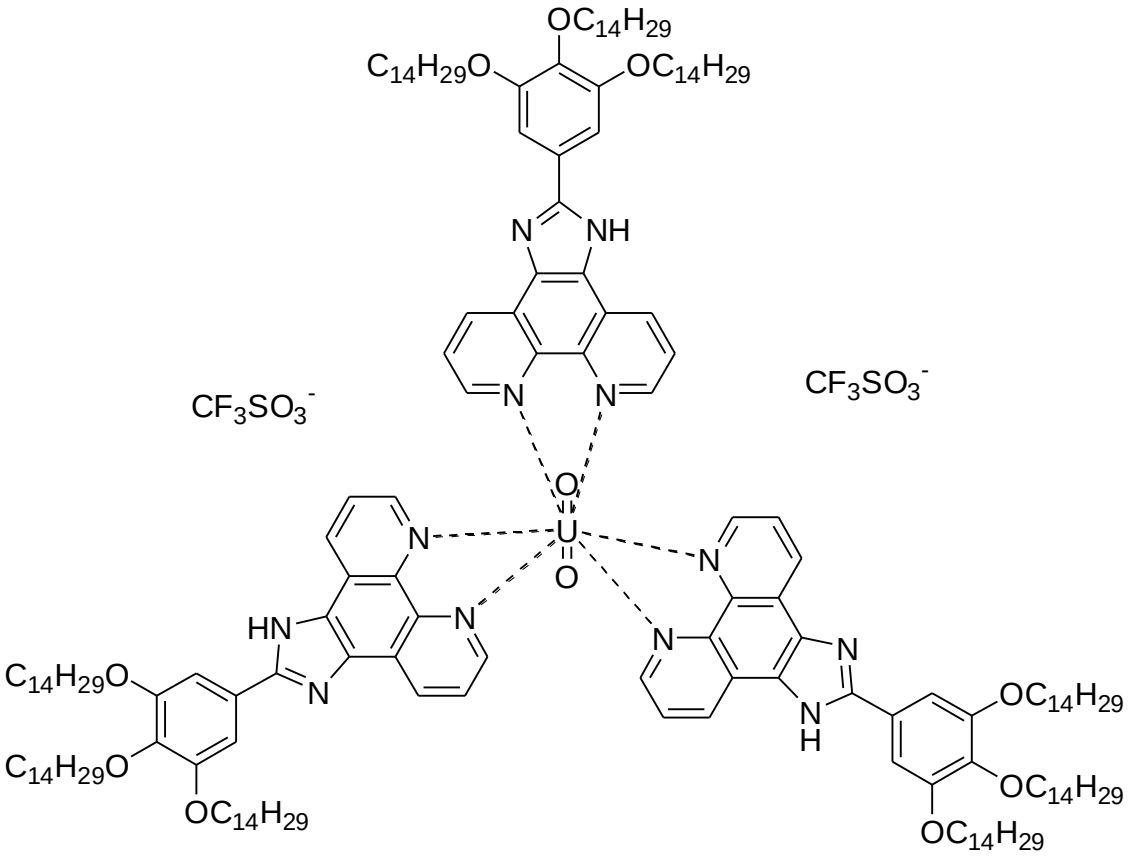
Cr · 181 · I

Nickel(II)



Liquid-crystalline (Col_h) from room temperature to > 300 °C

Dioxouranium(VI)



95 Col_h 181 I

Ref.: T. Cardinaels et al., *JACS* **127**, 17602-17603 (2005)

Conclusions

- Imidazo[4,5-f]-1,10-phenanthrolines are new type of ligands for liquid-crystalline metal complexes
  - the ligands can easily be substituted
  - substitution pattern allows to tune the mesophase behavior.
- Complexes can be made with a variety of metals: Ni(II), Cu(II), Pt(II), Pd(II), Re(I), Ru(II), Fe(III), Ln(III), U(VI)
- Decoupling of mesogenic and coordinating groups is possible
- Nematic phases observed for lanthanide compounds
- Rich mesomorphism including lamelllo-columnar phases

Acknowledgements

K.U.Leuven

- Thomas Cardinaels
- Jan Ramakers
- Dr. Kris Driesen
- Dr. Peter Nockemann
- Dr. Tatjana Parac-Vogt
- Prof. Dr. Christiane Görller-Walrand

IPCMS, Strasbourg

- Dr. Daniel Guillon
- Dr. Bertrand Donnio
- Dr. Cyril Bourgogne
- Dr. Benoit Heinrich